

"Nanocrystalline Processing and Interface Engineering of  $\text{Si}_3\text{N}_4$ -based Nanocomposites"

Technical Report on ONR Grant No. N00014-95-1-0626  
for the period of January 1, 1997 - March 31, 1997

Jackie Y. Ying  
St. Laurent Associate Professor  
Department of Chemical Engineering  
Massachusetts Institute of Technology  
Room 66-544, 77 Massachusetts Avenue  
Cambridge, MA 02139-4307  
Tel: (617) 253-2899  
FAX: (617) 253-3122

*Nanocrystalline TiN Sintering and Processing*

With careful powder handling procedures and processing, the nanocrystalline TiN produced in our novel reactor undergoes tremendous sintering and densification to produce dense (99%) TiN materials at 1400 °C in a simple, pressureless sintering process [1]. This quarter's efforts continued our work on the synthesis, sintering and processing of nanocrystalline TiN in five main areas [2]. The first area was the continued improvement of the valved filter collection device. The second area involved a study of the microstructure of the green bodies of the TiN materials, while the third focus was a study to quantify the amounts and types of gases evolved during the heating of nano-TiN which had been exposed to air for various amounts of time. The fourth focus area was on HIPing (hot isostatic pressing) of our nano-TiN, and the fifth area involved modeling the nitridation process of our Ti nanoclusters and comparing that system to the nitridation kinetics in the Si-Si<sub>3</sub>N<sub>4</sub> system.

Based on the previous results for sintering the air-exposed nano-TiN powders [3], a valved filter collection device had been previously added to our reactor to allow for powder removal from the reactor without exposure to air. Efforts this quarter focused on continuing to improve the efficiency of this unit. A variety of porous metals, metal felts and polymer-based membrane materials with various pore sizes were utilized in several configurations to optimize the yield of our collection process while continuing to satisfy the gas flow and operating pressure requirements of our synthesis process. High quality nano-TiN materials can be currently collected at a rate of 0.95 g/hr. This represents an increase of 240% in the collection rate from the previous quarter (0.4 g/hr) and an increase of 1890% over our first collection efforts using a liquid nitrogen cooled disc (0.05 g/hr). The evaporation rate of Ti in our reactor is 11.2 g/hr. Our collection rate of 0.95 g/hr of TiN means that 6.9% of this evaporated Ti is collected as TiN. Our reactor represents approximately a 10-fold increase over the production rates achievable in the traditional batch-type reactors for the synthesis of nanocrystalline materials. Additionally, the design of our reactor allows us to produce a variety of nanocrystalline nitrides (Si<sub>3</sub>N<sub>4</sub>, TiN, AlN). The batch-type reactors, limited to the production of nano-metals and nano-oxides, cannot synthesize these materials. One of the primary goals of this project was to design, build and demonstrate a process for scaling up the production rate of high quality nanocrystalline, nitride materials. This goal has been achieved.

In order to help explain the differences in sinterability of our nano-TiN as compared to commercially available TiN, pellets of each powder sintered at 800 °C (just at the onset of appreciable sintering) were examined via SEM and BET to determine the pore size distribution and structure. This characterization of the "green" bodies demonstrated the much narrower pore size distribution in our compacted nano-TiN as compared to compacts of the commercial TiN (Figure 1). This distribution resulted from the very narrow particle size distribution of our starting powders and is likely responsible, in part, for the enhanced sinterability of the nano-TiN.

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During the sintering process, a variety of adsorbed gases may evolve from the high surface area nano-TiN. If this evolution occurs at or near the onset of closed porosity, the potential for entrapment of these gases leading to decreased density is significant. Additionally, a large amount of adsorbed gases may significantly affect the reactivity of the surfaces and interfaces in the compacted nano-TiN. In order to measure the types of gases evolved during the sintering process, a mass spectrometer (Hewlett Packard Mass Selective Detector - HP 6890) was used to directly monitor the gases evolved during heating of the nano-TiN powder (5 °C/min under a flow of He). Weight changes were simultaneously measured in a thermogravimetric analyzer (Perkin Elmer Series 7 TGA). The exhaust stream was analyzed by the mass spectrometer. Nano-TiN samples which had been exposed to air for 5 minutes, 1 day, 2 days and 8 months were compared with a sample of the commercial TiN. The weight losses measured corresponded to the gases detected in various temperature ranges. For example, shown in Figure 2a is the weight loss versus temperature data for a nano-TiN exposed to the ambient atmosphere for 1 day. The mass spectrometer data for this sample is shown in Figure 2b. Initial weight loss corresponds to the volatilization of water (18) and adsorbed OH which ionizes to 16 (O) and 1 (H). [The 1 is not detectable in the mass spectrometer due to the use of He (2) as the carrier gas.] At 800 °C there is a sharper drop in weight corresponding to additional O and CO (28) evolution from desorbed carbonates. (Alternately, the 16 peak may be due to the evolution of CH<sub>4</sub>. The 28 is more likely to be CO than N<sub>2</sub> due to the very low amounts of N (14) detected as well as the fact that there is no corresponding increase in the 14 levels at 800 °C as the 28 levels are increasing.) The slight increase in 14 levels below 800 °C may be due to CH<sub>2</sub> removal. Above 800 °C, a contribution from N due to the decomposition of TiN is likely. During heating, water (18) was driven off at low temperatures, with the 18 signal disappearing at 600 °C. Above 1300 °C, additional water (likely chemisorbed) was liberated and detected. This raises the possibility that OH groups may be driven off above these temperatures thereby increasing the amount of titanium oxide formed in the sintered materials by leaving behind O to bond with Ti. In contrast, for the nano-TiN exposed only 5 minutes during sample loading, the only detected species was 14 (likely due to the decomposition of TiN with small amounts of CH<sub>2</sub> removal). The potential for CO, CH<sub>2</sub> and CH<sub>4</sub> evolution during heating of these materials is further supported by the fact that recent ESCA (electron spectroscopy for chemical analysis) measurements have detected 24.2 at% C on the surface of the air-exposed nano-TiN.

We have begun to study pressure-assisted consolidation processes (hot isostatic pressing (HIP)) of these materials with two primary goals. The first would be to further reduce the amount of oxygen in these materials by limiting even further their exposure to air through the glass-encapsulation required for HIPing. The second would be to process at slightly lower temperatures than the current 1400 °C required to achieve full density in an effort to produce an even finer grained TiN than our current process yields (140 nm). Because we are working with the goal of minimizing the time at elevated temperature, our experiments have yet to yield a fully dense HIPed sample. However, the results to date regarding the development of oxide phases in these materials are very encouraging. As shown in Figure 3, when sintering both the air-exposed nano-TiN (a) and the nano-TiN unexposed below 800 °C (b), appreciable amounts of a Ti<sub>3</sub>O<sub>5</sub> phase are crystallized upon sintering. In the air-exposed materials, this obviously is a result of their exposure to air during processing. Even after sintering at 800 °C in the furnace attached to the glovebox without exposure to air, the nano-TiN compacts still have a surface area of ~ 95 m<sup>2</sup>/g. Thus, when these samples are removed from the glovebox furnace and transferred quickly (~ 10 seconds) to the high temperature furnace, they adsorb oxygen which is incorporated into the sintered materials. However, the samples which are HIPed to 1400 °C (Figure 3c) show no evidence of this Ti<sub>3</sub>O<sub>5</sub> phase. Efforts are continuing to optimize the processing schedule to yield dense, HIPed TiN materials.

Finally, in an effort to better understand the kinetic processes occurring during the nitridation of the metal nanoclusters in our reactor, the expanding sharp interface model for gas-solid reactions was utilized. Other researchers have shown previously that for the formation of both TiN and Si<sub>3</sub>N<sub>4</sub>, diffusion of N thru

the continuous nitride product layer is the rate determining step. The time ( $\tau$ ) to complete this step can be modeled as

$$\tau = \frac{\rho_M r_o^2}{6 b D C_{N_2}}$$

where  $\rho_M$  is the molar mass of the metal,  $r_o$  is the original radius of the metal particle,  $b$  is the stoichiometric coefficient for the reaction of the metal plus nitrogen going to the nitride,  $D$  is the diffusivity of N thru the product layer and  $C_{N_2}$  is the surface concentration of nitrogen on the particle. For the reaction of either Si or Ti plus  $N_2$  going to the metal nitride, the values for the parameters above are essentially equivalent except for the diffusivity term,  $D$ . Due to the covalent nature of the bonding in  $Si_3N_4$ , diffusion of nitrogen is extremely slow. However, TiN is a primarily metallically bonded material, with much faster N diffusion. Using a temperature of 1200 °C (an estimate of the temperature in the plasma),  $D^N = 1.84 \times 10^{-21}$  cm<sup>2</sup>/s in  $Si_3N_4$ , while  $D^N = 8.59 \times 10^{-11}$  cm<sup>2</sup>/s in TiN. This leads to conversion times on the order of  $1.92 \times 10^{14}$  seconds for  $Si_3N_4$  particles and  $2.23 \times 10^3$  seconds for the TiN particles. However, both  $Si_3N_4$  and TiN undergo a volumetric expansion upon conversion from the metal, leading to a slightly microporous product layer with microcracks. This leads to a significant enhancement in the diffusivity of N, and thus, an effective diffusivity,  $D^{eff}$ , should be used in the above calculation.  $D^{eff}$  has recently been determined for N in the single particle conversion of Si to  $Si_3N_4$  [4]. We took some recent conversion data for the synthesis of TiN [5] and performed a similar analysis to determine  $D^{eff}$  for the conversion of Ti to TiN. At 1200 °C,  $D^{eff}$  in the  $Si_3N_4$  system is  $1.49 \times 10^{-10}$  cm<sup>2</sup>/s leading to conversion times of  $2.36 \times 10^3$  seconds. At this same temperature,  $D^{eff}$  in the TiN system for N is two orders of magnitude faster,  $1.41 \times 10^{-8}$  cm<sup>2</sup>/s, leading to a calculated conversion time of 13.6 seconds. Given that the change in free energy per mol  $N_2$  is more than 3 times as negative in the TiN system as it is in the  $Si_3N_4$  system (-391 kJ vs. -119 kJ), the local temperature at the particle surface is likely much in excess of the 1200 °C used in the above calculations. (Experimental evidence of this is seen in the fact that upon evaporation of Ti, and subsequent reaction to TiN, the pressure in the reactor increases causing the throttle valve to the vacuum pumps to open ~5° to maintain a constant pressure and compensate for the increase in temperature.) Additionally, the reaction is taking place in a plasma of activated N species. Thus, the actual conversion times we observe in our reactor are much faster; however, the above modeling demonstrates how differences in the chemical bonding of the two systems studied can impact their respective conversion times and explains the difficulties we have had in synthesizing fully converted, stoichiometric  $Si_3N_4$  in our reactor.

### Summary

Significant improvements to the filter collection unit have been made allowing us to collect materials at a rate of almost 1 g/hr. The greatly enhanced sinterability of our nano-TiN is likely due in part to its very narrow pore size distribution in the green state. A TGA/mass spectrometer study tracked the gases evolved from nano-TiN exposed to air for various times. These gases have an impact on, and can be correlated to, the sinterability of these materials. HIPing has eliminated the formation of the  $Ti_3O_5$  phase in the sintered nano-TiN. Modeling of the metal/nitrogen reaction has explained the differences in the synthesis of TiN and  $Si_3N_4$  in our reactor.

### References

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5. H. Rode and V. Hlavacek, "Detailed Kinetics of Titanium Nitride Synthesis," *AIChE Journal* **41** (1995) 377-388.

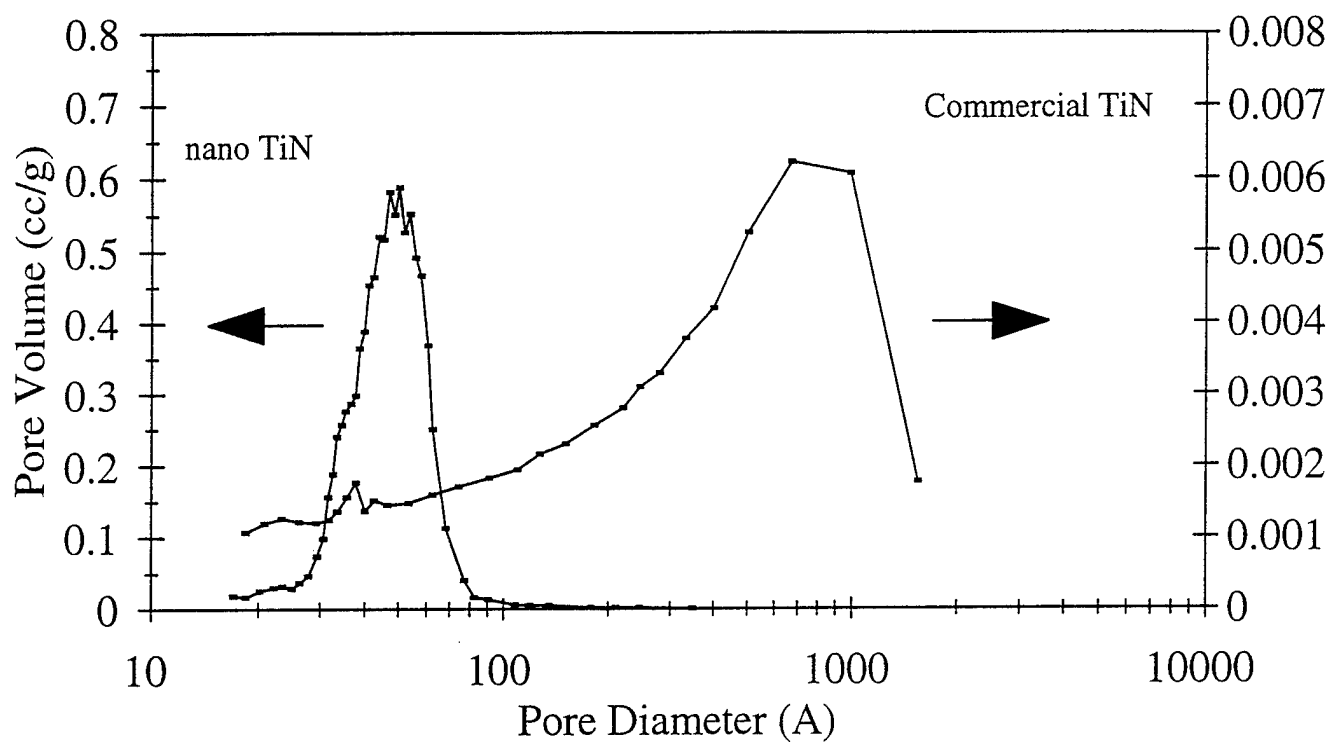


Figure 1: BJH pore size distribution of nanocrystalline and commercial TiN compacts sintered at 800 °C

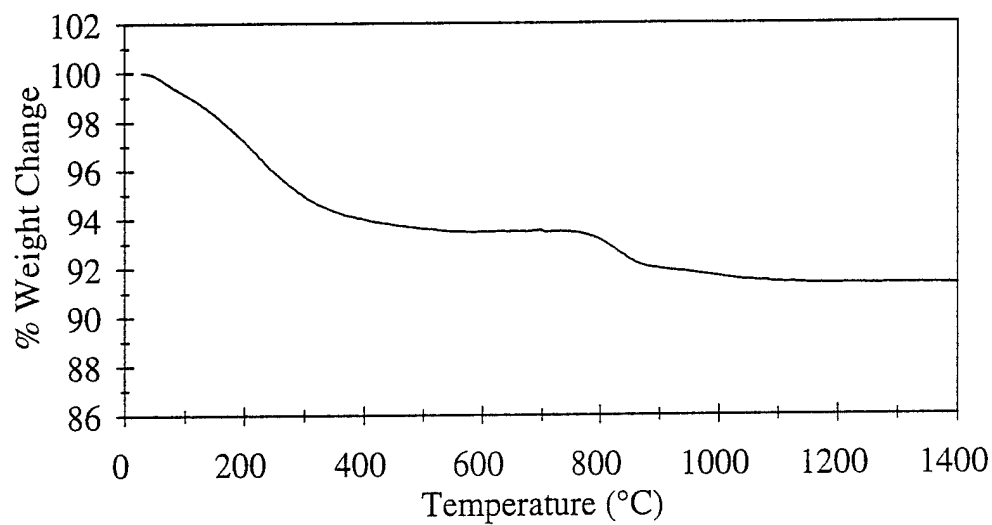


Figure 2a: TGA data for nano-TiN exposed 1 day

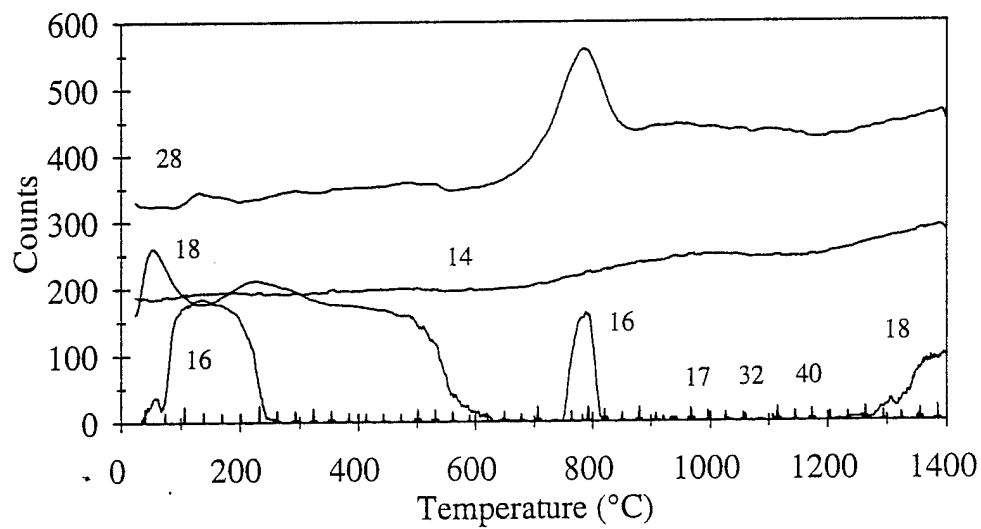
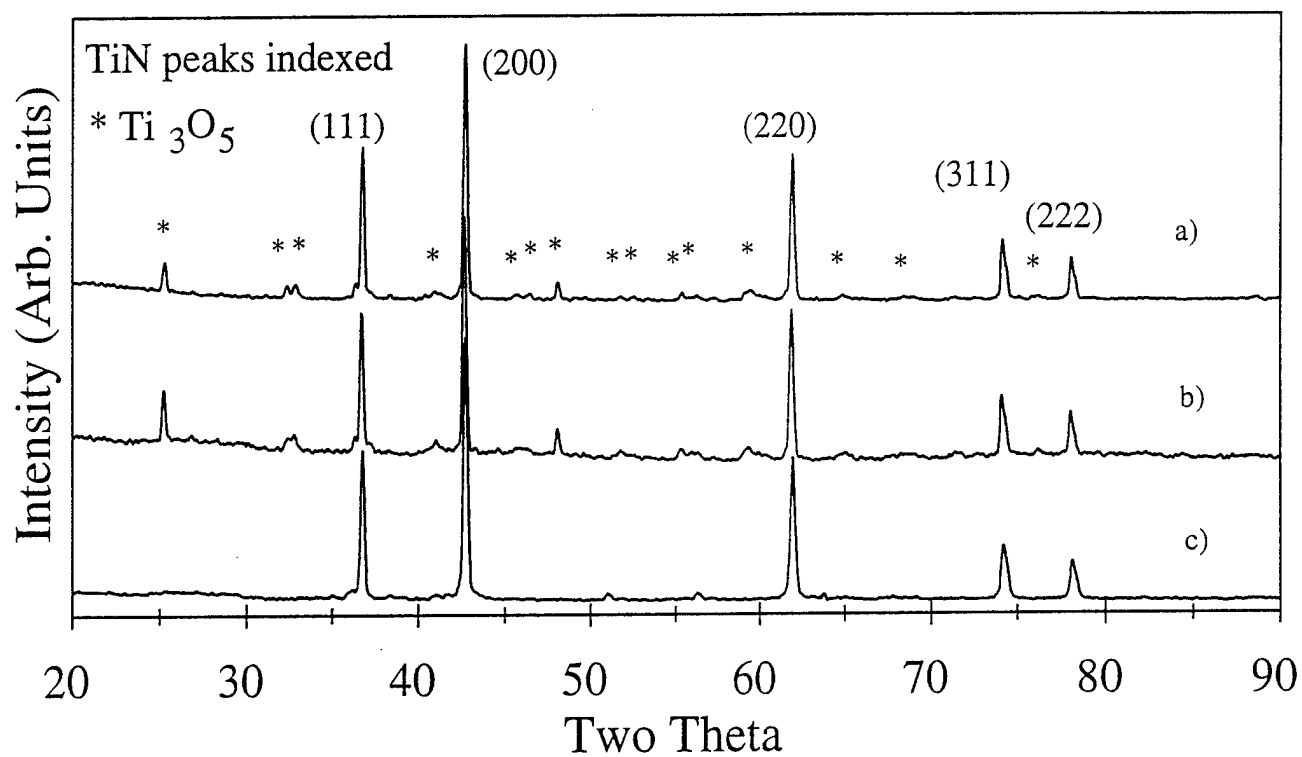


Figure 2b: Mass Spectrometer data for nano-TiN exposed 1 day



**Figure 3:** XRD data for sintered nano-TiN (a) exposed to air, (b) unexposed below 800 C and (c) unexposed below 1400 C - HIPed

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1 Apr 97		3. REPORT TYPE AND DATES COVERED Progress Report 1 Jan 97 - 31 Mar 97
4. TITLE AND SUBTITLE  Synthesis and Processing of Nanocrystalline Titanium Nitride			5. FUNDING NUMBERS  G - N00014-95-1-0626	
6. AUTHOR(S) Jackie Y. Ying				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemical Engineering Massachusetts Institute of Technology 77 Massachusetts Avenue, Room 66-544 Cambridge, MA 02139-4307			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Ballston Tower One Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) With careful powder handling procedures and processing, the nanocrystalline TiN produced in our novel reactor undergoes tremendous sintering and densification to produce dense (99%) TiN materials at 1400 °C in a simple, pressureless sintering process. This report outlines our continued work on the synthesis, sintering and processing of nanocrystalline TiN. Improvements to the filter collection unit in our reactor continue to be made. A SEM/BET study of the microstructure of the green bodies of the TiN materials was completed. A TGA/Mass Spectrometer study quantified the amounts and types of gases evolved during the heating of nano-TiN which had been exposed to air for various amounts of time. HIPing (hot isostatic pressing) experiments of our nano-TiN continued and demonstrated the potential for a reduction in the oxide content of the final, sintered materials. Modeling of the nitridation process of our Ti nanoclusters and a comparison of that system to the nitridation kinetics in the Si-Si <sub>3</sub> N <sub>4</sub> system was performed.				
14. SUBJECT TERMS Nanocrystalline Processing, Titanium Nitride			15. NUMBER OF PAGES 7	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	